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Silt Geochronology and Mineralogy, Mount Daisen, Japan

Afshan Shaikh
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SILT GEOCHRONOLOGY AND MINERALOGY, MOUNT DAISEN, JAPAN

by

AFSHAN SHAIKH

Under the Direction of W. Crawford Elliott, Ph.D.

ABSTRACT

The mineralogy and geochronology of silt fractions were determined for a representative Andisol (volcanic soil) from the Mt. Daisen area as well as for collected bulk reference fallout materials from Japan, and Kyoto dust samples. X-ray diffraction techniques and K-Ar methods were used to determine the age values and mineralogy of test materials. The reference fallout material was the youngest (21 Ma). The Kyoto dust was oldest (210 Ma) of all materials. The silt from the Andisol yielded older age values closer to the top and younger values closer to the parent tephra. The silt mineralogy revealed small amounts of 10 Å and 14 Å phases. The presence of these phases in the silt fractions of soils having parent dactic-basaltic tephra (<1 Ma) combined with the geochronology ages of the silt fraction (21 – 210 Ma) support the hypothesis that there is an aeolian influence present in the Andisol.

INDEX WORDS: Japan, Loess, Andisol, K-Ar, Geochronology, Dust, Soil
SILT GEOCHRONOLOGY AND MINERALOGY, MOUNT DAISEN, JAPAN

by

AFSHAN SHAIKH

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

in the College of Arts and Sciences

Georgia State University

2015
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2015
SILT GEOCHRONOLOGY AND MINERALOGY, MOUNT DAISEN, JAPAN

by

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May 2015
DEDICATION

I would like to dedicate this thesis to my family for showing me the value there is in education. I hope to make you proud and continue to be a student of knowledge throughout my life.
ACKNOWLEDGEMENTS

This research was a collaborative study in which I was honored to work with some great minds: Dr. Crawford Elliott of Georgia State University, Dr. Marion Wampler of Georgia Institute of Technology (retired), Dr. Atsushi Nakao of Kyoto Prefectural University, and Dr. Junta Yanai of Kyoto Prefectural University.

I like to acknowledge Dr. Elliott’s patience with taking on a graduate student that had no background in geochemistry or mineralogy into a world that was dense in both. I learned a great amount about from him and am grateful to have had him as an advisor while at Georgia State University.

I like to acknowledge Dr. Wampler’s willingness to take me under his wings and share his K-Ar methods with me and help me get an excellent grasp on the chemistry and math that takes place when conducting geochronology.

I like to thank Dr. Nakao and Dr. Yanai for their willingness to work and collaborate with our team overseas and for answering all my questions, and helping understand papers that were in Japanese.

I would like to thank Dr. Nadine Kabengi for teaching me about the instrumentation behind all of the machinery required to do my research and for her willingness to be on my committee.

I would like to thank Nathan Rabideaux and Lucy Mejia for helping me with my scans and helping me get the programs I needed to be able to analyze my data.

Thank you Georgia State University for providing me with the teaching assistantship and stipend each semester that allowed me to do this research.
Lastly, I would like to acknowledge the NSF grant XRD 1029020, without which this work could not have been completed.
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1 INTRODUCTION

Japan is a tectonically active sub-continent. It is located at the intersection of 4 tectonic plates: Eurasian, North American, Philippine and Pacific. A convergent boundary is found east of Japan marking the contact between the Eurasian Plate and two oceanic plates (Pacific and Philippine). The Pacific Plate and the Philippine Plate are both subducting below the Eurasian-Amurian plate. The directions of the tectonic plates are shown in Figure 1.

The Pacific Plate is moving west and the Philippine plate is moving northwest. This tectonic setting has shaped the country, allowing for accretionary, metamorphic, and volcanic processes to occur (Geological Survey of Japan, 2014). The basement rock of Japan is oldest toward the west side of the Japan. The ages of these rocks range from middle to late Paleozoic (Wakita, 2013). In northeastern areas of Japan, the age of the basement rock is not clear due to

Figure 1. Tectonic Activity of Japan (www.numo.or.jp).
(The red star indicates the location of Mt. Daisen)
the very thick volcanic deposits and sediments that were deposited on bedrock during the Neogene (Geological Survey of Japan, 2014). The active tectonics and volcanism play a vital part in many surface processes that occur within Japan. At the outset, the focus of this thesis will be a study of the volcanic soils at Mt. Daisen.

This tectonic setting explains the relatively large number of volcanoes (ten percent of the world’s volcanoes) on Japan while consisting of only 0.25 percent of the world’s land surface (Web of Japan). In terms of presently active volcanoes, there are eighty-six active volcanoes. Approximately 21 more volcanoes will be considered active in the near future (Japan Meteorological Agency, 2001). Figure 1 shows the locations of the volcanic fronts (arcs) of Japan. Mt. Daisen is located 100 km northwest of the of the southwest Japan arc at approximately N35°22’42”, E133°30’41”. Tephra is the predominant parent material of the soil in the Mt. Daisen region, resulting in the formation of widespread volcanic soils (Andisols). The parent tephra deposits have been tested using absolute dating methods and have yielded age values of less than 1 Ma (Nakao, personal communications, 2015).

1.1 Andisols

The predominant soil order found in Japan is Andisol. According to both Japanese soil taxonomy and USA soil taxonomy, Andisol is a soil that forms from volcanic ash parent materials (Nanzyo et al., 2007). Andisols are formed by rapid weathering of volcanic tephra and ash, and in situ formation of noncrystalline materials from the weathered ashes and tephras (Nanzyo et al., 2007). Two main types of Andisols are observed in Japan, those with allophane and those without allophane.

Figure 2. Major Regions of Japan (Japan-guide.com).
(nonallophanic). Allophane is secondary weathering product of volcanic glass. The International Committee on Classification of Andisol claims the central idea of this soil order is that it is a soil developed from volcanoclastic material and ejecta, where the colloidal fraction is composed of short range order minerals and aluminum (Al) humus complexes. The Japanese Cultivated Soil Classification defines Andisol soils as having developed in pyroclastic materials. They have, low bulk densities, high phosphate adsorption coefficients and high “fluffiness” (Takahashi and Shoji, 2002).

In terms of early observations on Andisols, this soil order was established after finding nonallophanic material in soils formed by volcanic ash in Japan (Takahashi and Shoji, 2002). The root of the world Andisol means dark (an) soils (do) in Japanese. This soil order was once characterized as a subgroup of inceptisols but was reclassified as of 1978. This soil order is very important for agriculture in Japan. Cultivated Andisols, used for agriculture, account for almost one third (1.35 million hectares) of the total land used for crop production in Japan (Takahashi and Shoji, 2002). Andisols are widely distributed in the regions of Hokkaido, Tohoku, Kanto and Kyushu. These regions (Figure 2) are where most of the volcanism is located (NUMO, 2015).

Soil properties of Andisols have unique properties relative to other soil orders. Nanzyo et al, 2007 summarized the important soil properties of Andisols. Per Nanzyo et al. (2007), Andisols are dark in color. They are light, fluffy, and easily broken into smaller pieces. The permeability is very high. As these volcanic soils become older, the macropores within the soil decrease and micropores increase, but still maintain a macropore space of 10 percent. This permeability allows both water and air to flow easily into the soil, making it suitable for plant growth. Their colloidal fraction is very reactive given their high surface area. Chemically, Andisols are different from other soils because they are rich in Al. The high aluminum
concentrations in these soils comes from the leaching and removal of other elements and the retention of Al as oxides as these soils are being formed. Mineralogically, Andisols are quite different from their parent materials. The primary constituents in tephra deposits include: volcanic glass, plagioclase, hornblende, olivine, quartz, biotite, and opaque minerals. The most abundant mineral in volcanic ash is colored and noncolored volcanic glass. The pedogenically formed minerals in soils and volcanic ashes typically are predominantly allophane, imogolite, Al and Fe phases, and short range order minerals. These minerals are essential for crop production. Allophane is a secondary mineral with fine spherical morphology allowing water to easily pass through. Imogolite, another secondary mineral, has a more tubular structure. Halloysite is present and allows for high cation exchange capacity for potassium (K) (Nanzyo et al., 2007).

1.2 Climate and Prevailing Winds

The climate varies greatly in Japan. The north-south extent of Japan extends 25 degrees in latitude. The relief of the country is 3776 meters. The highest elevation is at Mt. Fuji (Web of Japan). The climate of the Japan ranges from subarctic to subtropical. The west side of the islands are characterized by moist winds from the Asian continent, which are stopped by the mountainous terrain in the center of Japan (Japan Meteorological Agency, 2014). During the spring time, cyclonic wind patterns bring strong winds from interior Asia. The Japan Meteorological Agency (JMA) continuously monitors a mineral dust being brought over by the westerlies, giving them the name “Kosa.” These material comprises the fraction of loess and other fine grained minerals originating elsewhere than Japan. The compositions of these sediments are described in Section 1.3. The specific field site investigated, Mt. Daisen, is located in the Tottori Prefecture within the Chogoku region. In this region, prevailing winds come from
Siberia during the winter season. During the summer season, the prevailing winds come from the Pacific ocean.

1.3 Loess and Aeolian Dust Background

Loess can be any aeolian sediment that has been entrained, transported, and deposited by wind and is dominated by silt-size particles (Muhs, 2013). The silt deposits composed of either loess or aeolian dust are most likely to have silicate minerals such as quartz, feldspar, mica, and clay and carbonate grains (Pye, 1987). Phyllosilicate clays (smectite, chlorite, mica and kaolinite) are also present in loess (Muhs, 2013). Loess can vary in size, being smaller than aeolian sand (2000 - 50 \( \mu \text{m} \)), and larger than aeolian dust (<10 \( \mu \text{m} \)) (Muhs, 2013). Loess is typically found within the silt fraction (2-50 \( \mu \text{m} \) in diameter), with smaller amounts present of clay and sand (Muhs, 2013). Concerning the grain size distribution, the most common grain size is 20-40 \( \mu \text{m} \) skewed toward having finer particles (Pye, 1987). Aeolian mineral dusts collected in Japan contain quartz, muscovite and certain other minerals commonly absent from young Japanese volcanic rocks but present in soils (Andisol) formed on these rocks (Inoue and Naruse, 1987; Baustita-Tulin and Inoue, 1997). The late Quaternary volcanic rocks underlying Mt. Daisen are less than 1 million years old (0.02-0.15 Ma, Nakao, personal communication, 2014) while K-Ar and Ar-Ar dating has shown micaceous material from Asian dust to be more than 100 million years old (Dymond et al., 1974; Pettke et al., 2000).

The precise composition of any given dust is dependent on the nature of the source material. Coarse-grained dusts are usually rich in quartz, feldspar and carbonate minerals. Far-traveled dust typically contains micas and clays (Pye, 1987). In Beijing, China, the dominant constituents in windblown dust were quartz and mica and the other minerals found in lesser amounts were feldspars, chlorite, calcite and amphibole. Loess deposits found in Jiuzhoutai,
China, are composed of more than 5% each of quartz, feldspar, calcite and illite and chlorite (Pye, 1987).

As part of the JMA monitoring, the JMA posts “Kosa” advisories. Kosa, an aeolian dust, is monitored by collection of particulates from air samples. The sediment, as defined by the JMA, is “composed of mineral particles moved by frontal activity from semi-arid areas of the Asian continent and transported by westerly winds to Japan.” Kosa is monitored regularly during the year. The regions of Chugoku, Shikoku and Kyushu (Figure 2) are all characterized by having yellow skies and haze in the spring season (March, April, May) because of the strong cyclonic winds moving aeolian sediment eastward. Other regions of Japan are also receiving these westerly winds, but not to the extent as the three regions mentioned.

The monitoring data from 1981 to 2010 shows better the occurrences of Kosa (Figure 3). The highest average number of days in a given month in which Kosa was observed was 9 (Figure 3). Figure 3 provides an idea of the annual variation of number of monthly Kosa events, the most being April in mid-spring. The lowest number of events were noted in the late summer and early fall (Japan Meteorological Agency). Uematsu et al., (1983) confirmed in their study that
the transport of atmospheric dust displays a strong seasonal correlation; they noted also that the largest deposition occurred in the spring time.

1.4 Accidental Release of Radionuclides from Fukushima-DaiichiReactors

Radionuclides pose a major health and contamination issue for a given region when they are accidentally released into the environment. However, understanding the nature of the radionuclides released and their interactions with the environment is vital to predict the fate of these radioactive contaminants. The Fukushima Nuclear Power Plant (FDNPP) in particular, released a considerable inventory of radioactive contaminants (primarily volatile radioactive Cs and I) into the Fukushima Prefecture from March 11, to April 2011. Nuclides detected in soils include: $^{129}$Te, $^{129m}$Te, $^{131}$I, $^{134}$Cs, $^{136}$Cs, $^{137}$Cs, $^{140}$Ba, $^{140}$La, and possibly $^{99m}$Tc and $^{110}$Ag (Endo et al., 2012; Kato et al., 2012; Tanaka et al., 2012). The average activity ratio of $^{134}$Cs/$^{137}$Cs (corrected to April 1, 2011) for three different soils at Koriiyama, Fukushima Prefecture is 0.980 ± 0.004 (Ohno et al., 2012). The amounts released were $1.3 \times 10^{16}$ Bq of $^{137}$Cs and $1.5 \times 10^{16}$ Bq $^{131}$I (Chino et al., 2011). Only a very low fraction of the reactor core was released based on the measured $^{237}$Pu released from FDNPP (Bossew, 2014). Presently, significant and measurable amounts of radiocesium ($^{137}$Cs) remain as the primary radioactive contaminant affecting the Fukushima Prefecture (Figures 4,5). Radioiodine has decayed due to it short half-life ($t_{1/2}$ of $^{131}$I is 8 days). $^{134}$Cs has also a short half-life (2 years). Thus, these latter two radionuclides are not considered as long-term contaminants in the Fukushima Prefecture outside the FDNPP reactors. Ambient radioactivity is measured in the soils within the Fukushima Prefecture. One sample studied in this thesis was collected from a soil from the Fukushima Prefecture. The radioactivity of a nearby soil was 0.27 µSv h$^{-1}$ (0.03mR h$^{-1}$ or 0.3 R/y).
$^{137}\text{Cs}$ in soil samples studied after the nuclear accident revealed that 90% of the radionuclide was present in the top 5 cm of soil (Yoshida, 2012). Studies of $^{137}\text{Cs}$ show that it is favorably sorbed into the wedge zones within the interlayers of weathered micaceous minerals (e.g. Nakao et al., 2008, 2009). The weathering of mica produces frayed edge sites. As frayed edge sites develop, K escapes and is replaced by strongly hydrated cations. $^{137}\text{Cs}$ is favorably sorbed due to its size and charge into the wedge zone. Once fixed into these weathered micaeous minerals, $^{137}\text{Cs}$ migration does not occur. It is fixed within the weathered material. The provenance of the weathered materials fixing $^{137}\text{Cs}$ in these soils is thought to be aeolian material from interior Asia. The aeolian material would explain the presence of micaceous minerals and clays present within Andisols. The Andisol has a dacitic composition and would not contain any mica or weathering products of mica.

The Mt. Daisen area is studied as the field site for this preliminary study. Mt. Daisen was not contaminated by radionuclides that were released from the Fukushima nuclear disaster. However, the aeolian material sorbing the $^{137}\text{Cs}$ in the Fukushima prefecture is likely to be found in the Mt. Daisen area. By collecting material from a site that was not contaminated, we can study the aeolian material without concern for radioactive contamination. Mt. Daisen and Fukushima are will contain similar material within their silt fraction. Thus by understanding the aeolian presence within Andisol in Mt. Daisen, a better understanding of the material sorbing $^{137}\text{Cs}$ in Fukushima will be had.
Figure 4. Deposition of Cs-134 and Cs-137 showing the NW trajectory from FDNPP (Yoshida and Takahasi, 2012).

Figure 5. Decrease in radioactivity in soils over a one year period within Fukushima Prefecture. The left panel was data collected and mapped in October 2011. The right panel shows radioactivity approximately 1.5 years later. The radioactivity decreased on average from 3-4 $\mu$Sv h$^{-1}$ to $< 1$ $\mu$Sv h$^{-1}$. This decrease in radioactivity reflects the decay of $^{137}$Cs (Tsukada, 2014).
1.5 Hypothesis and Expected Results.

For the past 50 years, it is well known that illite or weathered mica can sorb radiocesium at frayed edge sites (e.g. Nakao et al., 2008, 2009a, 2012, 2014 and references therein). Illite and micaceous phases are thought to be present in Andisols of Japan. However, the Japanese volcanic rock is of dacitic-basaltic composition, which is quite different than the felsic minerals such as illite and albite found within the Andisols (Nanzyo, 2002; Nanzyo et al., 2007). The micaceous minerals sorbing Cs are hypothesized to be aeolian in origin. The purpose of this study is to test the hypothesis that the micaceous component is aeolian in origin and originating from the Asian continent and further that aeolian minerals make up a measurable component in the Mt. Daisen Andisols. The testing of this hypothesis will provide an increased understanding of the source of aeolian minerals being deposited at Mt. Daisen. Such micaceous minerals are thought to play an important role in fixation of radiocesium accidentally released from the FDNPP reactors. An implication of our hypothesis is that, were it not for phyllosilicates contributed by aeolian processes, radiocesium in Japanese volcanic soils (Andisol, in particular) could be relatively mobile (more available for leaching and uptake by plants). In such a case, modeling the behavior of the radiocesium would require much more specific information about soil characteristics than if that behavior were controlled by aeolian micaceous soil components. These data will help to derive a predictive model to explain the fixation of the released radiocesium in these soils. This information will be beneficial in land use, such as farming and ensuring human health and safety when concerned with contaminants fate.

From the foregoing, it is expected that there is a significant presence of aeolian material present within the Andisols of Japan based on results of Bautista-Tulin and Inoue (1997), Muhs
The transported aeolian dust from Asia is a significant source of sedimentary addition in the North Pacific Ocean (Uematsu et al., 1983; Pettke et al., 2000). It is estimated that the deposition rate of the dust during February-June in the 25 – 40° N latitude is 2.3 to 5.6 x 10^6 tons/year (Uematsu et al., 1983). It is likely that the aeolian material will be mineral dust containing significant amount of quartz and illitic and micaeous material (Pye, 1987; Muhs, 2013; Bautista-Tulin and Inoue, 1997). The silt and clay fraction from the volcanic soils collected from within the Mt. Daisen region are of Quaternary age. It is predicted that if K-Ar analysis is performed on the silt fraction, the absolute ages will indicate the presence of a component that is older than the bedrock tephra from Mt. Daisen. Such older material is predicted to aeolian materials from interior Asia (Bautista-Tulin and Inoue, 1997). Dusts in the northcentral Pacific sourced to the Gobi desert indicated source components with ages of ~ 200 Ma or older in the studies by Pettke et al. (2000) and Stevens et al. (2010). The age of Mt. Daisen aeolian component is estimated to be ~ 200 Ma.

## METHODS

### 2.1 Field Work for Mt. Daisen

Soil samples were collected near Mt. Daisen on August 7, 2013 at a location of N35°22'42.29", E133°30'41.29. There were five samples collected of no more than 100 grams of soil each. These samples were collected from the top 1.35 meters from a pit dug by Prof. Kadono and students (Tottori University, Japan). The samples were taken from depths of 0-33 cm, 33-58 cm, 58-72 cm, 72-100 cm and 100-135 cm (Figure 6). At a depth greater than 1.35 meters, the material is the unaltered parent tephra. The horizons visible are A-Horizon organic soils from 0-100 cm and C-Horizon altered volcanic ashes from 100 – 135 cm. Nakao tentatively
identifies the sample collected at 58-72 cm to be either A or C horizon. The age of the parent is < 1 Ma (Prof. Nakao, personal communication, 2014).

![Mt. Daisen Soil Profile](image)

**Figure 6. Mt. Daisen Soil Profile.**

### 2.2 Sample Preparation for Mt. Daisen Soil

When the samples arrived in the laboratory, they were unaltered from the original site of excavation. First, the soil color was determined using a Munsell Soil Color Chart. Once the soil colors were identified for the 5 sections they were heated at 50°C for 24 hours to remove moisture. The Munsell Color Chart was used again to note any changes in color. A sample splitter was then used to divide the sample into four equally distributed portions. Two of the four portions were used for materials from the 0-33 cm section and 33-58 cm section. These materials were labeled 1A, 1B and 2A and 2B, respectively. Only one portion was used for the 58-72 cm portion and was labeled 3A.
Table 1. Name Assignment for Test Material

<table>
<thead>
<tr>
<th>Test Material (cm)</th>
<th>Name Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-33</td>
<td>1</td>
</tr>
<tr>
<td>33-58</td>
<td>2</td>
</tr>
<tr>
<td>58-72</td>
<td>3</td>
</tr>
<tr>
<td>72-100</td>
<td>4</td>
</tr>
<tr>
<td>100-135</td>
<td>5</td>
</tr>
</tbody>
</table>

One sample of each soil was treated by methods of Jackson (1979) to remove the cementing agents and to disperse effectively the sample soil. The cementing agents such as carbonates and amorphous iron oxides were removed through various chemical treatments. Removal of the carbonates was accomplished through a treatment using 1 N sodium acetate (NaOAc), and acetic acid buffer (pH = 5) (see appendix A.1). Next, the soils were treated with 30% hydrogen peroxide, H$_2$O$_2$, to oxidize and to remove organic material and aid in mineral colloid dispersion (Appendix A.2). Finally a sodium citrate-sodium bicarbonate-sodium dithionite (Na$_2$S$_2$O$_4$) mixture, abbreviated CBD, was used to remove free iron oxide cements from soil (Appendix A.3). The removal of amorphous iron oxides is accomplished to some degree by the CBD method. The removal of these oxides and cements permits better size fractionation into sand, silt and clay fractions (Jackson, 1979). Once the chemical treatments were done, timed settling was used to separate the different size fractions. The size fractions obtained by timed settling using deionized water were: <2µm; 2-5 µm; 5-20µm; > 20 µm fractions (Jackson, 1979). The > 20 µm fraction is largely quartz by inspection with binocular microscope. Oriented mounts of clay and silt fractions (except > 2 µm) were made for sample in
preparation for X-ray diffraction (XRD). For the K-Ar preparation, the 5-20 µm sized test material was used. Portions 1A and 2A were analyzed twice, with the extra trial including stepped heating.

2.3 Dust Preparation

2.3.1 Kyoto Dust Preparation

The dust samples were prepared for K-Ar age determinations in Japan by Dr. Atsushi Nakao at the Kyoto Prefectural University (Figure 7). The material was collected at an altitude of 100 meters using water-dust suspension methods (Nakao, personal communication, 2015). The total area of collection was 3.2m² and is conducted monthly. For this study, samples from March and May were used because of the well-known dust storms, entitled “Kosa” as discussed in Chapter 1, occur in the spring months. Once the dust had been collected, it was allowed to settle for 24 hours and then water was removed. The material was treated with 10% hydrogen peroxide at 80-90°C to remove organics per A. Nakao, 2014. The remaining material was also saturated with NaCl solution to remove exchangeable potassium. Following drying, the dust samples were screened to sizes of <2 µm, 2-20 µm, 20-50 µm, 50-200 µm, 200-2000 µm. The test material from Kyoto Prefectural University was the 2-20 µm size fraction of dust sample collected March 6, 2013 and May 6, 2013. There was 205 mg of the March sample and 209 mg of the May sample (Prof. Nakao, personal communication, 2015). For the K-Ar work, the 2-20 µm size fraction of the dust sample collected from March was given the name AS1B. The material from May was given the name AS1C.
2.3.2 Reference Fallout Material Preparation

The reference fallout material was prepared by the Meteorological Research Institute of Japan. It is a combination of collected material that was created to be a reference material for airborne fallout. The material was collected from 1963-1979 from 14 stations around Japan (Otsuji-Hatori et al., 1996). The fourteen stations are shown in Figure 8 below. The material was pulverized and then passed through a 150 mesh screen; each sample contains material less than 100 µm. The three samples were labeled 2-21, 8-6 and 8-36. Each contained about 210 mg of material. The sample that was used for K-Ar analysis was 2-21. However, all three reference fallout materials were scanned using XRD.

Figure 7. Image of Kyoto Dust (Two left) and reference fallout material used in K-Ar dating.
2.4 K-Ar Methods

The decay of radioactive elements creates clocks based on probabilistic decay from parent to daughter in a given period of time (e.g. $^{40}$K to $^{40}$Ar). In K-Ar dating, the unstable parent nuclide is potassium-40 ($^{40}$K). If this isotope is enclosed in a rock or mineral during the time of formation or crystallization, and if the rock or mineral has not been altered with respect to the introduction or change of K or argon (Ar), then it is expected that the radiogenic daughter products of the $^{40}$K, e.g. ($^{40}$Ar) will be retained within the rock or mineral. $^{40}$K has a branched decay where approximately 11 percent of the decay is to $^{40}$Ar and 89 percent is to $^{40}$Ca. The $^{40}$K
and $^{40}$Ar atoms are measured and the amounts are used to calculate the K-Ar age of the test material. Faure and Mensing (2005) reviewed the K-Ar geochronologic technique.

### 2.4.1 Potassium Analyses

To determine the potassium concentrations within samples, approximately 10 mg of each sample were weighed out. Material was then digested using a combination of nitric acid (HNO$_3$) and hydrofluoric acid (HF) for approximately 8 hours. After digestion, the containers were opened to allow evaporation of strong acids and leaving behind nitrate salts. The residual matter left after evaporation was mixed with a dilution solution (0.01 M CsCl and 0.1 M HNO$_3$). These solutions, as well as K standards were used to test whether K concentrations were within the optimum range for measurement by atomic absorption spectrophotometry (AAS). If any test solution was not within that range, more dilution solution was added.

Many methods can be used to find the concentrations of potassium, such as AAS and inductively coupled plasma (ICP) spectrometry. In this work, AAS (Figure 9, 10) was preferred over ICP-MS$^1$. ICP-MS uses Ar as a carrier gas. Thus, it would be difficult to distinguish Ar from K in the mass spectrometer by this method. A potassium hollow-cathode lamp was operated at 6 mA. Absorption within the flame was measured at a wavelength of 766.5 nm. The absorption of the K in AAS is such that any absorption reading between 0 and 0.5 is within range where the relationship between concentration and absorbance is linear. This linear relation permits the accurate determination of the concentration of K in the test solutions and allows the determination of the mass fraction of K in the test materials. The unknown solutions and samples of known K concentrations are run in order of increasing K concentration, and then in decreasing

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$^1$ ICP-MS is Inductively Coupled Plasma-Mass Spectrometry
order. Thus, the unknowns are bracketed between known samples. This minimizes potential drift from the heating in flame atomic absorption readings. This also minimizes effects of memory from previous sample (Figures 9).

2.4.2 Argon Isotope Analyses.

The argon isotopic compositions of the unknown samples were determined by using isotope-dilution-mass spectrometry at GSU\(^2\) following procedures established by Dr. Wampler of Georgia Institute of Technology. In the use of isotope dilution-mass spectrometry, a precise amount of purified \(^{38}\)Ar of known Ar isotopic composition (i.e. a spike) is added to the gases and all gases extracted from a sample. This added spike makes it possible to determine quantitatively the amount of \(^{40}\)Ar extracted from this sample.

Samples were weighed into a copper capsule (shown below, Figure 11) using a Denver Instruments M-220 analytical balance in 310 KH\(^3\). This balance is accurate to the 0.3 milligram.

\(^2\) Georgia State University.

\(^3\) 310 Kell Hall is the laboratory used to conduct the research. It is located on GSU Campus.
The capsules were loaded into the Ar extraction line and the line was brought to vacuum. Before the radiogenic Ar was extracted, all samples except 1A and 2A were pre-heated at approximately 180°C with a small electrical resistance heater surrounding the sleeve containing the samples. The purpose of the pre-heating was to release atmospheric Ar from the test material (Figures 12, 13). The test materials were then, one by one, melted at high temperature using an electrical resistance furnace to release all gases from the sample material. The spike with $^{38}$Ar of known amount and isotopic composition was added to the gases released, and the mixed gases were passed through a trap by liquid nitrogen. Gases that condense at liquid nitrogen temperatures ($\text{H}_2\text{O}, \text{CO}_2$) were thus removed from the extracted gases. Heated titanium getters were used to eliminate all other reactive gases (methane). The purified gas and spike mixture was analyzed by a MS-10 mass spectrometer in the static mode. Based on the amount of $^{38}$Ar, it was then possible to calculate the total $^{40}$Ar in this sample. Once the amounts of $^{40}$K and radiogenic argon were found, the values can be used in an equation as shown below. The equation will give an answer in the unit of years. For the exact lab procedures please refer to the Appendix B. These procedures are similar to those used in previous K-Ar age determinations at GSU (Osborn et al., 2014; Elliott et al., 1999).

$$^{40}\text{Ar} = \frac{\lambda_e}{\lambda} ^{40}\text{K}(e^{\lambda t} - 1)$$

$^{40}$Ar = the amount of $^{40}$Ar present after time t  

$^{40}$K = the amount of $^{40}$K atoms after time t  

$\lambda_e$ = the decay constant of $^{40}$K to $^{40}$Ar  

$\lambda$ = the total decay constant of $^{40}$K  

$\text{t} = \text{time}$
e = the base of natural logarithms

For the exact lab procedures please refer to the appendix B.

Figure 11. Image of copper capsule used to contain test material in K-Ar determination.

Figure 12. Image of 5 samples in copper capsule.

Figure 13. Preheating of samples using electrical heater.

2.4.3 Error of K-Ar Measurements

The error associated with the K-Ar geochronologic measurements is estimated from the sum total of individual errors. These individual errors include estimated error associated with the composition of the $^{38}$Ar spike, weighing errors, mass spectrometry analyses, and error in the potassium analyses. In aggregate and where sufficient radiogenic argon is measured, this error is
estimated for approximately < 5% of the age measured. Error is estimated to be much larger for samples whose percentage of radiogenic Ar was low (< 10%). These errors are as high as 15-20%. These errors result from the difficulty to measure low amounts of radiogenic Ar relative to atmospheric Ar.

2.5 X-Ray Diffraction Methods

X-ray diffraction is a technique that is used to help characterize the mineralogy of fine crystalline particles and clays. This technique was used to characterize the mineralogy of the reference fallout material, the Kyoto dust samples and the Mt. Daisen silt samples. A Panalytical X’Pert Pro X-ray diffractometer was used in this study.

X-rays are produced at the anode of an X-ray generating tube. To create X-rays (white radiation and characteristic radiation), electrons are accelerated from the tungsten filament into the anode (Cu). A negative high voltage between a tungsten filament and a copper anode (- 45 KV) accelerated the electrons as they are boiled off the tungsten filament by the application of a small current (40 mA). As these electrons are accelerated from the filament to a Cu anode, these electrons strike the Cu anode resulting in the release of lots of heat, white radiation, and X-rays characteristic of the Cu anode. The resulting characteristic X-rays from the Cu anode are collimated to the test material. Copper Kα radiation is the incident radiation (Cu Kα, 1.54 Å) used in this study.

If the test material is solid, has a crystalline internal structure, and if Bragg’s Law is satisfied, then the X-rays will be diffracted from the sample. The samples are scanned through a range of diffraction angles 2θ. A pattern is produced showing the intensities of diffracted radiation as a function of 2θ. Bragg’s Law is stated below:

\[ n\lambda = 2ds\sin\theta \]
Where \( \lambda \) is the wavelength of the incident radiation, \( d \) is the spacing between atomic layers of the test material, and \( \theta \) is the angle between the incident radiation and the slide containing the test material. Once a pattern is produced the \( d \) value can be calculated for each diffracted peak knowing the wavelength of incident material \( \lambda \), and the angle of incidence \( \theta \). The set of measured \( d \) value are then interpreted to identify the minerals present (Moore and Reynolds, 1997). In all of the XRD scans, a graphite monochromator aft of the sample position was used to filter reflections arising from CuK\( \beta \) radiation diffracted from the sample.

For the Mt. Daisen test material <2 µm, approximately 4 ml of slurry containing < 2 µm fraction was pipetted onto petrographic glass slide until the slide was completely covered with the test material. The slide was then left to air dry. Another identical slide was made, but then glycol solvated for 24 hours after it was dried. The analysis of a glycol-solvated sample is needed to identify swelling clays (smectite) within the test material. A third slide was made identical to the air dried sample was heated to 500° C for 60 minutes was also conducted to aid in mineral identification. These slides were scanned from 3-32°, \( 2\theta \). A divergence slit of 0.0625° was used for the <2 µm and the 2-5 µm fractions.

For the 5-20µm Mt. Daisen fractions, reference fallout material, and the Kyoto dust samples, randomly packed powder scans were conducted using circular sample holders. For the Mt. Daisen 5-20 µm samples, compacted rotational holders were used. However for the dust and reference fallout material, zero background holders were used because only approximately 200 mg of was sample available (Figure 14, 15). All of the randomly packed samples were analyzed at a speed of 1°/2 min from 5°-60° \( 2\theta \) with a divergence slit of 0.5°. Then all of the XRD results were analyzed using Panalytical High Score software to determine the best matches for each pattern.
Figure 14. 5-20µm bulk sample disk.

Figure 15. No Background Scan Disk with reference fallout material
3 RESULTS

3.1 K-Ar Age Values

K and radiogenic Ar ($^{40}\text{Ar}^*$) were measured, and the age values calculated, for the Mt. Daisen fines silt, the Kyoto dust, and reference fallout material are listed in Table 2 below.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Description</th>
<th>K (% by mass)</th>
<th>$^{40}\text{Ar}^*$ (%)</th>
<th>$^{40}\text{Ar}^*$ (µmol kg$^{-1}$)</th>
<th>K-Ar age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS1A</td>
<td>Reference Fallout Material</td>
<td>1.38 ± 0.05</td>
<td>9.5</td>
<td>51 ± 9</td>
<td>21 ± 4</td>
</tr>
<tr>
<td>AS1B</td>
<td>Kyoto Dust 3.4</td>
<td>1.59 ± 0.05</td>
<td>72.1</td>
<td>612 ± 13</td>
<td>210 ± 8</td>
</tr>
<tr>
<td>AS1C</td>
<td>Kyoto Dust 5.6</td>
<td>1.08 ± 0.03</td>
<td>46.9</td>
<td>253 ± 10</td>
<td>130 ± 6</td>
</tr>
<tr>
<td>1A (5-20 µm)</td>
<td>0-33 cm</td>
<td>1.65 ± 0.08</td>
<td>8.3</td>
<td>181 ± 17</td>
<td>62 ± 6</td>
</tr>
<tr>
<td>1B (5-20 µm)</td>
<td>0-33 cm</td>
<td>1.96 ± 0.10</td>
<td>3.4</td>
<td>183 ± 14</td>
<td>61 ± 5</td>
</tr>
<tr>
<td>2A (5-20 µm)</td>
<td>33-58 cm</td>
<td>1.66 ± 0.08</td>
<td>4.1</td>
<td>109 ± 61</td>
<td>27 ± 15</td>
</tr>
<tr>
<td>2B (5-20 µm)</td>
<td>33-58 cm</td>
<td>1.70 ± 0.09</td>
<td>19.6</td>
<td>114 ± 16</td>
<td>34 ± 5</td>
</tr>
<tr>
<td>3A (5-20 µm)</td>
<td>58-72 cm</td>
<td>1.92 ± 0.10</td>
<td>8.6</td>
<td>101 ± 18</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>1A (5-20 µm), Preheated</td>
<td>0-33 cm</td>
<td>1.65 ± 0.08</td>
<td>27.6</td>
<td>174 ± 11</td>
<td>60 ± 5</td>
</tr>
<tr>
<td>2A (5-20 µm), Preheated</td>
<td>33-58 cm</td>
<td>1.96 ± 0.10</td>
<td>74.1</td>
<td>96 ± 5</td>
<td>28 ± 2</td>
</tr>
</tbody>
</table>

The measured K-Ar age value of the reference fallout material AS1A was 21 Ma. The Kyoto dust samples 3.4 and 5.6 yielded age values of 210 Ma and 130 Ma, respectively. The age values for the silt fractions of the Mt. Daisen soils decreased from about 60 Ma for the uppermost sample to ~ 30 Ma for the next two samples going downward. Three determinations
on silt from the material on top, from 0-33 cm, yielded consistent age values of 62 Ma, 61 Ma, and 60 Ma. At a depth of 33-58 cm, three determinations gave age values of 27 Ma, 34 Ma, and 28 Ma, but relatively large error values mean there is no significant difference in the three determinations. The age value of 30 Ma for silt collected from the soil at 58-72 cm (sample 3) is not significantly different from the values for sample 2.

3.2 XRD Results and Munsell Color

The Munsell soil color for test material 1 (0-33 cm) was 3/2 7.5YR, for test material 2 (33-58 cm) was 2.5/1 5YR and test material 3 (58-72 cm) was 3/2 7.5YR. The soil samples were size separated and randomly packed powder XRD scans were ran for 5-20 µm fraction. Oriented glass slides were run for 5-20 µm and <2 µm fractions. Slides of 2-5 µm size faction were prepared, but the slides were not suitable for XRD scans due to curling of the test materials as they dried. The scans of the three portions of reference fallout material (Appendix C.1) showed distinct peaks at for quartz (4.26 Å and 3.33 Å), halite (2.81 Å, 1.98 Å), albite (4.02 Å, 3.19 Å), and hematite (3.66 Å, 2.68 Å). The presence of a calcium sulfate was evident in all three samples as well. These peaks indicate the presence of gypsum or anhydrite in these reference fallout materials. For reference fallout material 8-36, the diffraction data was more consistent with anhydrite (3.49 Å, 2.84 Å). For reference fallout material samples 8-6 and 2-21, the diffraction data were consistent with gypsum (3.74 Å, 2.82 Å). The diffraction data for the Kyoto dust (Appendix C.2) test material showed distinct peaks at quartz, albite, 10 Å clay, and trace 14 Å clays.

Scans of the randomly packed 5- 20 µm (i.e. fine silt) from the Mt. Daisen Andisol (Appendix C.3) also showed clear peaks for quartz and albite consistently for the three samples ranging in depth from 0-72 cm in this profile. A peak at 8.3 Å was not identified. A 10 Å peak
was seen in the 33 -58 cm sample of the profile. The diffraction peaks of the oriented fine silt (5- 20 µm) fractions did not shift appreciably after glycol solvation for the 0-33 cm, 33-58, and 58-72 cm samples. On heat treatment at 500°C, the 14 Å was no longer present.

From the < 2 µm oriented slides (Appendix C.4), it was found that there were clear peaks for quartz, albite, and a 14 Å clay for the samples encompassing 0-72 cm of the profile. The 2-5 µm slide for only one soil sample was suitable for XRD scans. This yielded clear quartz and 14 Å clay peaks.

4 DISCUSSION

4.1 Reference Fallout Material

It was expected that K-Ar analysis of the reference fallout material would yield age values that are greater than 100 million years (Dymond et al., 1974; Pettke et al., 2000). However, an age of 21 Ma was determined. The XRD patterns combined with ICP-AES results

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP-AES (mg g⁻¹)</th>
<th>ICP-MS (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.53 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>41.45 ± 0.51</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>11.60 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>26.03 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>7.58 ± 1.43</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>63.06 ± 0.51</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>11.38 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.80 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>31.24 ± 0.40</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>8.69 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>4.51 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.26 ± 0.06</td>
<td>264 ± 2</td>
</tr>
<tr>
<td>Ca</td>
<td>0.37 ± 0.00</td>
<td>5.62 ± 0.05</td>
</tr>
</tbody>
</table>

Errors are SD of triplicated measurements.

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4 Inductively Coupled Plasma- Atomic Emission Spectroscopy
from Otsuji-Hatori et al., 1996 show the major mineral constituents of reference fallout material 2-21, 8-6, and 8-36 all contained distinct peaks corresponding to quartz, halite and feldspar peaks. Calcium sulfate was also present in the reference fallout material as either gypsum or anhydrite. In reference fallout material 8-36 anhydrite (CaSO$_4$) was present. In reference fallout material 8-6 and 2-21, there were gypsum (CaSO$_4$. 2H$_2$O). In regard to elemental contributions from minerals, the largest amounts of Na and Ca present within the reference fallout material can be attributed to the halite, calcium sulfate, and feldspars present. The contribution of K is likely from K-feldspars and any micas present (biotite). Hematite was identified in reference fallout material 8-36 and 8-6, which would identify a major contributor of the iron present. Biotite peaks were identified in all three peaks and is a likely contributing to the large Mg and Fe and potentially K (Otsuji-Hatori et al. 1996). These reference fallout materials were aggregated from individual samples collected from stations throughout Japan from 1963 to 1979 (Otsuji-Hatori et al., 1996). These samples were screened using a 150 mesh (100 µm) screen. The measured K-Ar age value of reference fallout material 2-21 was quite young (21 Ma). If this age value is representative of similar material elsewhere in Japan, then the progenitor of this reference fallout material is more likely to be a better representative of the local material of Japan instead of materials transported from interior Asia given data from Dymond et al (1969) and Pettke et al (2000).

The lack of selective seasonal sampling opens the possibility that this reference fallout material is less representative of the observed silt fraction mineral dust found in the Mt. Daisen Andisol and perhaps Andisols present elsewhere in Japan (Bautista-Tulin A.T., Inoue, 1997). The changes in wind patterns with seasonal cycles allow for the addition of materials from multiple sources, including sea spray processes. NaCl present from sea spray could mean a
potential K contribution as well. The chemical composition of typical ocean water contains 1.1% dry weight of K (UGS, 2015). The concentrations of K produced by Otsuji-Hatori et al. (1996) could likely be a combination of K from sea salts in addition to weathered sediments containing K. If the material is far-traveled from Asia, it is expected to be enriched with finer sized material, such as clays (Pye, 1987). There were no clear clay peaks present in any of the reference fallout material XRD patterns. Trace amounts of 1:1 clay, perhaps kaolinite, might be present in reference fallout material 2-21, but it is not with great confidence. Only 200 mg were available for each reference fallout material sample, no treatments were done following the preparation from the Meteorological Institute of Japan. If the material was size separated and oriented mounts were made for XRD scans, then a better understanding of the material could be had. The age values of the reference fallout material likely represents a mixture of K derived from sea salt, aeolian material, and local soil material.
4.2 Kyoto Dust Material

XRD analysis of the Kyoto dust was performed at both GSU (Appendix C.2) and KPU\(^5\).

KPU conducted XRD analysis on K-saturated and Mg-saturated slides for the March and May Kyoto dust (Figure 16). At GSU, XRD scans were done with zero background holders on randomly packed powder of both samples. The randomly packed powder XRD patterns showed trace amounts of 10 Å and 14 Å clays. The material of the Kyoto dust was 2-20 \(\mu\)m. For optimal scans using randomly packed powder, a size between 5 to 10 \(\mu\)m is recommended (Moore and Reynolds, 1997). However, the scans were still conducted to ensure consistency of information with KPU. The XRD scans from KPU provided clear 7 Å, 10 Å, and 14 Å peaks. Dr. Nakao, who performed the analysis, estimated the concentration of mica content present within the Kyoto dust. For the March material, he calculated an amount of 11.1g/kg and for May it was

\[\text{[mica concentration]}\]

\[^5\text{Kyoto Prefectural University, located in Kyoto Prefecture, Japan.}\]
calculated that there was 7.1g/kg present within the dust. Given the age value and mineralogy, the Kyoto dust samples are a good representative of the aeolian material that would be coming from interior Asia. The known collection location and time of collection allows for more confident inferences of the material. Kosa events are most abundant in mid-spring. These samples were collected in March and May, which are peak times for Kosa. Thus, this material is likely to be more characteristic of the aeolian material that is being brought in to Japan than the reference fallout material.

4.3 Andisols

The mineralogy from the randomly packed powder scans did not show a significant change throughout the soil layers. Each layer had distinct quartz, plagioclase feldspar, and 14 Å peaks. The best matches for feldspar peaks were albite. In slide 2B from the 33-58 cm section, there was a 10 Å peak. In the <2 µm slides, the mineralogy did not change throughout the soil profile. There were clear 14 Å, quartz, and albite peaks. Only the sample 2B from 33-58 cm section of the profile was scanned for the 2-5 µm fraction. Other slides from this fraction were not adequate for scanning because of cracking and extensive peeling. Scans of 2B showed 14 Å and quartz peaks, and with less certainty calcite peaks. The 10 Å peaks are interpreted to be illite/muscovite. The 14 Å clays is vermiculite or chlorite because the oriented glass slides were glycol solvated and no noticeable shift occurred in the scans when compared to the air dried scan. Upon heating to 500°C, the 14 Å peaks were no longer present, which asserts the 14 Å clay is vermiculite. The presence of similar felsic minerals within the fraction can be attributed to the relatively young soil and the process of deposition of aeolian material. The formation of the tephra deposits after volcanic events would mean there would be no aeolian material in the parent tephra. The aeolian material would be present after the formation of tephra deposits and
would therefore be present in the soils above the parent tephra material. During pedogenesis of the Andisol, the aeolian material would be continuously worked into the soil as well as continuously deposited on the top of the soil profile. Therefore, the addition of aeolian material would be from the top of the soil profile and would explain why the ages are significantly older towards the top. If soil formation processes occur while at the same time as aeolian deposition, then it would be expected that the material would be present throughout the soil depending on the paleoclimatic patterns and amounts of aeolian deposition. For example, Pettke et al., (2000) suggests over the past 12 Ma years the flux of dust in the North Pacific increased an order of magnitude due to a drying in central Asia.

4.4 K-Ar Age Values

K-Ar determination yielded age values of 21 Ma for the reference fallout material and 130 Ma and 210 Ma for the Kyoto dust samples for March and May, respectively. The difference in age values can be attributed to the collection process of each of the sample. The reference fallout material was an amalgamation of solids obtained by drying collected wet and dry deposition from all over Japan, from multiple years. The reference fallout material was prepared in an attempt to get an average of the radioactive fallout across Japan. The reference fallout material was not chemically treated to remove exchangeable K and other cations. However, the Kyoto dust samples were collected from a known location and time. They were collected at Kyoto Prefectural University in March 2013 and May 2013. They were treated with hydrogen peroxide and saturated with Na to remove exchangeable K. One of the concerns in interpreting the K-Ar age value of the fallout material is that owing to the small sample size, no chemical treatments were done to it before K-Ar determination. Another concern is the potential that sea salts may be present within the material. The XRD patterns of the reference fallout material show
NaCl within the material. The presence of NaCl means there is a possible K contribution from sea salt. Typical ocean water contains 1.1% of K by dry weight (UGS, 2015). These sea salts could become airborne by bursting bubbles in the ocean, or even waves crashing against each other or crashing on surfaces. The sea salt K would have produced no radiogenic Ar, resulting in an age value less than the age value of silicate dust in the fallout material. All of the collection stations for the fallout material are near the sea (Figure 8). Therefore, there could be quite a bit of influence from sea spray processes. If the contribution from the sea salt could be determined, then the age value could be corrected, accordingly.

The K-Ar age value of the silt fraction from Mt. Daisen was greatest for the uppermost of the Mt. Daisen soil samples. The significant decrease of the age value with depth might be indicative of weathering processes within the Andisols whereby relatively more young silt-sized K-bearing material has been lost from the feldspar in the uppermost part of the horizon. That idea can be tested petrographically, using an optical microscope to verify the mineralogy. Another explanation for a difference in the age values is that the age values reflect a mixing between silt-sized particles of the tephra (< 1 Ma) and the aeolian silt fraction. The dacitic tephra contains K-bearing phases. This K adds to the K from the aeolian material but there is no corresponding addition of radiogenic Ar. The source of K is not discriminated by AAS analyses. If the aeolian silt were mixed with silt from dacitic tephra, then the resulting ages would be reduced.

K-Ar analyses were performed on the soil silt fractions to test the idea that some of the silt had provenance outside of Japan. These K-Ar determinations were done with no knowledge of any mixing between any parent tephra and the minerals in the soil silt fraction. It is possible that there may be mixing between the Andisol soil minerals and the parent tephra.
Table 4. Description of soil profile from Mt. Daisen, Japan (Nakao, personal communication 2015).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Horizon Name</th>
<th>Depth (cm)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Ex-K cmolc/kg</th>
<th>Allophane g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS1</td>
<td>A1</td>
<td>0-33</td>
<td>23.6</td>
<td>50.7</td>
<td>25.6</td>
<td>0.143</td>
<td>77.1</td>
</tr>
<tr>
<td>DS2</td>
<td>2A</td>
<td>33-58</td>
<td>22.3</td>
<td>56.2</td>
<td>21.4</td>
<td>0.090</td>
<td>23.4</td>
</tr>
<tr>
<td>DS3</td>
<td>2AC</td>
<td>58-72</td>
<td>25.1</td>
<td>54.5</td>
<td>20.4</td>
<td>0.053</td>
<td>48.2</td>
</tr>
<tr>
<td>DS4</td>
<td>3A</td>
<td>72-100</td>
<td>20.4</td>
<td>46.4</td>
<td>33.2</td>
<td>0.100</td>
<td>25.2</td>
</tr>
<tr>
<td>DS5</td>
<td>3C</td>
<td>100-135</td>
<td>17.9</td>
<td>57.4</td>
<td>24.7</td>
<td>0.096</td>
<td>222.0</td>
</tr>
</tbody>
</table>

Another factor that may be relevant is the change in the flux of aeolian material deposited in Japan during the time it took for this soil to develop. Further investigation is needed, but a change in wind intensity or direction over the past one million years would change the amount of aeolian material deposited. A change in amount of aeolian deposition could explain the greater age value toward the top of the soil. A short term intense wind event could even contribute significantly to the soil and cause changes in the K-Ar ages.

Another concern about the K-Ar dating was the unusually large amount of atmospheric Ar found in the Mt. Daisen fine-silt samples, which caused relatively large uncertainty in their K-Ar age values. To reduce the amount of atmospheric Ar, duplicate portions of samples 1A and 2A were preheated at ~280°C overnight before radiogenic Ar was extracted at much higher temperature. Most of the atmospheric Ar in each of these test portions was driven out during the preheating. Dr. Marion Wampler hypothesized that the large amounts of atmospheric Ar were trapped in secondary minerals within the soil samples. Both allophane and imogolite are weathering products of volcanic glass. These phases are hydrous aluminosilicates with little structural ordering. While Figure 17 shows that the Mt. Daisen area does not have much allophane within the soils, an analysis by Dr. Nakao shows that there is still a significant concentration of allophane. The amount of allophane in the Mt. Daisen soil profile ranged between 23.4 g/kg to 222 g/kg. Imogolite often occurs in soils as a mixture with allophane. The presence of imogolite and allophane may provide explanation of the large amounts of...
Atmospheric Ar released from the Mt. Daisen silt samples. Allophane nanoparticles are spherical, while the structure of imogolite nanoparticles is cylindrical. Atmospheric Ar that was dissolved in soil solution probably became trapped along with water inside allophane nanospheres.

K-Ar age values from the earlier, but the reduction in amount of atmospheric Ar mixed with the extracted radiogenic Ar led to improved accuracy of the age values. However, if done again to ensure there is no significant alteration from the allophane and imogolite, then using oxalate dissolution to eliminate all of the imogolite and allophane from the test material is suggested. In a method of dissolution by acid oxalate solution, Higashi et al., (1974) suggested a method of dissolving allophane without being detrimental to the delicate clay minerals.

![Figure 17. The distribution of allophanic and non-allophanic Andisol (Takahashi and S.Shoji, 2002).](image-url)
5 CONCLUSIONS

Geochronologic analyses have shown the silt from Mt. Daisen Andisol, Kyoto dust, and reference fallout material were all significantly older compared to the known age value of the parent tephra (< 1 Ma). This aeolian material is of vastly different mineralogy compared to the dactic-basaltic composition of the parent tephra soil. K-Ar results of the reference fallout material yielded age values much younger than expected (21 Ma). XRD analysis revealed NaCl that may have skewed the age values by the addition of excess K from sea spray processes. K-Ar determination on Kyoto dust yielded age values of 130 Ma and 210 Ma for March and May, respectively. The Kyoto dust is concluded to be a better representative of the aeolian material, “Kosa” influencing the Andisols rather than the reference fallout material. K-Ar values from the silt fraction at different depths in the soil profile yielded different values. Interestingly, it was shown that the 0-33 cm age values were significantly older (60 Ma, 61 Ma, 62 Ma). The 33-58 cm age values yielded ages of (27 Ma, 28 Ma and 34 Ma). The 58-72 cm section yielded an age value of 30 Ma. This difference in age with depth in the soil profile may provide insight into the weathering process of Andisol and the chemical processes that occurs with the addition of aeolian material. The 10 Å and 14 Å clays are being added to the Mt. Daisen Andisol. This conclusion is supported by the dacitic composition of the parent tephra relative to the felsic composition of these clays. It is believed that these clays are being deposited as aeolian material. This study was preliminary work that will be used to get further knowledge into the soil chemistry of Mt. Daisen. The work at Mt. Daisen is preliminary to understanding the role(s) of aeolian phases in the fixation of radionuclide Cs-137 contaminant released from the FDNPP.
REFERENCES


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6 This email summarized a paper that was in Japanese.


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http://scholarworks.gsu.edu/geosciences_diss/4
Appendix A: Jackson Treatments

Carbonate Treatment A.1

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Weigh out 20 g of the sample and add to 1000ml beaker.</td>
<td>20 minutes prep time.</td>
</tr>
<tr>
<td>2. Add about 100 ml of NaOAc to breaker and stir</td>
<td>4 hour bath. (maybe overnight)</td>
</tr>
<tr>
<td>3. Cover in plastic wrap and secure with rubber band</td>
<td></td>
</tr>
<tr>
<td>4. Place in water bath at 50°C for 4 hours</td>
<td></td>
</tr>
<tr>
<td>Do the same procedure for 20 g of the same sample once more.</td>
<td></td>
</tr>
<tr>
<td><em>Best to react in same solution overnight. Negative pressure should be seen.</em></td>
<td></td>
</tr>
<tr>
<td>5. Then mix the samples and for each of the 20 gram samples, separate them into two centrifuge tubes each. (For a total of 4 to centrifuge). Chase them with NaOAc. When you are treating four samples at one time, then you will chase into one centrifuge bottle using about 50 ml of buffer.</td>
<td>1 hour</td>
</tr>
<tr>
<td>6. Centrifuge. Setting on 8 minutes, speed of 1100.</td>
<td></td>
</tr>
<tr>
<td>7. Decant the liquid from all four of the tubes into one beaker and label it as the CO3 removal leech.</td>
<td></td>
</tr>
<tr>
<td>8. Wash with NaOAc, mix and centrifuge.</td>
<td></td>
</tr>
<tr>
<td>9. Do #8 again.</td>
<td></td>
</tr>
</tbody>
</table>
### Peroxide Treatment A.2

<table>
<thead>
<tr>
<th>Procedures</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Add 10ml of peroxide sample at 30 minute intervals. Repeat this for a total of 50ml of peroxide.</td>
<td>Actual mixing takes like 10 minutes, wait time is at least 30 minutes. Minimum wait time is 2.5 hours.</td>
</tr>
<tr>
<td>Keep a thermometer in there to see if there is a significant change in temperature.</td>
<td>Wear protective gear, eyewear, gloves, and coat.</td>
</tr>
<tr>
<td>2. Cover the solution in a beaker and add to water bath at 50C. Chase with small amounts of 30% hydrogen peroxide.</td>
<td>Leave overnight.</td>
</tr>
<tr>
<td>3. Leave overnight. There is usually a distinct color change</td>
<td>Leave overnight</td>
</tr>
<tr>
<td>4. Wash sample with NaOAc and centrifuge</td>
<td></td>
</tr>
<tr>
<td>6. Wash with methanol and centrifuge. As mentioned before, please save all washing together in one beaker or plastic bottle.</td>
<td></td>
</tr>
</tbody>
</table>

### Iron Oxide Treatment A.3

<table>
<thead>
<tr>
<th>Procedures</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pour out methanol into waste container</td>
<td>1.5 hours to 2 hours.</td>
</tr>
<tr>
<td>2. Warm up water bath</td>
<td></td>
</tr>
</tbody>
</table>
| 3. Add to sample:  
  40ml of 0.3 Na-citrate 
  5ml of NaHCO₃ |               |
| 4. Sit in bath for 15 minutes                                            |               |
| 5. Add 1g dithionite, stir for one minute. Wait for two minutes.     |               |
| 6. Do #5 two more times.                                                |               |
| If needed, for the last 5 minutes add methanol to help flocculate. |               |
| 8. Wash samples with NaOAc twice (save the decanted liquid as iron oxide removal) and then Methanol. | |
Appendix B: K-Ar Methods

Weighing B.1

Containers

| 1. | Select or prepare a copper-foil capsule for each sample to be analyzed for argon isotopes. | No special precautions are needed to avoid contamination in handling the copper capsules, but they must be kept free of extraneous rock or soil dust that would contain radiogenic argon. |
| 2. | Place the set of capsules in a holder so that each capsule can be distinguished from the others by its position within the holder. | It is not convenient to label the capsules, but it is convenient to associate each capsule with an identified position in the sample holder. The identifying letters and/or numbers may be used in forming the "test portion identifiers" needed to distinguish the weighed test portions from one another (and from members of all other sets of weighed test portions). |
| 3. | Select a clean PFA container for each sample to be used for potassium determination. | Containers should have been washed in detergent solution, then rinsed well with tap water, and then finally rinsed with de-ionized water. The containers should not be completely dry, so static electric charges may be avoided. |
| 4. | Label each PFA container so it can be distinguished from the others in the set. | It is convenient to use for each PFA container the identifier (letter, number, or combination) associated with the corresponding copper capsule. |

Weighing

| 5. | Set an appropriate balance to zero. | Taring cannot be used in this procedure. All mass values must be relative to a zero setting obtained with nothing on the balance pan. Frequent re-zeroing is good practice, unless a special procedure for increased accuracy, described at the end of this document, is used. |
| 6. | Weigh an empty copper capsule. Record the mass as that of the ‘Empty capsule.’ | It is good practice to check each mass value after it has been written down. It will not be possible to check any mass value after the analyst has gone on to the next step of the weighing procedure. |
| 7. | Put in the capsule an amount of material appropriate for determining the potassium content of the material. | It is essential that what is put in the capsule be an unbiased sample of the larger sample of material whose argon isotope and potassium contents are to be determined. |
| 8. | Weigh the capsule and its contents. Record the mass as that of the ‘Capsule plus first test portion.’ | In the end, the copper capsule will hold the test portion for argon isotope determination, but here the same capsule is used temporarily for weighing the test portion to be used for potassium determination. |
| 9. | Holding the capsule with special self-closing forceps, empty the contents of the capsule into the appropriate FEP container. | Be careful that static charge on the FEP container doesn’t cause loss of fine particles during transfer. It isn’t necessary that all of the material go into the FEP container. Any material that may cling to the inside of the copper capsule will become part of the test portion for argon isotope determination. |
| 10. | Weigh the capsule. Record the mass as that of the ‘Capsule after transfer of the first test portion.’ | This mass value will be greater than the originally determined mass of the empty capsule if any particles remained inside the capsule after the transfer. |
11. Put in the capsule an amount of the sample appropriate for the argon isotope determination.  

| It is essential that what is put in the capsule be an unbiased sample of the larger sample of material on which argon isotopes and potassium are to be determined. |

12. Weigh the capsule and its contents. Record the mass as that of the ‘Capsule plus second test portion.’

| This test portion includes any material that remained in the capsule when the test portion for potassium determination was transferred to PFA. Such material has become part of the test portion for argon isotope determination. |

13. Close the capsule by flattening the open end and folding it over. Then crumple the capsule, with care to avoid loss of material, as necessary to reduce its size.

| No part of the closed capsule should be more than ¼ inch across. |

14. Reweight the capsule.

| This is to account for any material lost when the capsule was crumpled. |

Repeat Steps 5 through 14 for each sample of material on which argon isotopes and potassium are to be determined.

**Drying and re-weighing (an optional procedure for clay-bearing materials)**

15. Dry the set of test portions for argon isotope determination, each test portion within its capsule and identified by the position of the capsule within the holder.

| The recommended method of drying is by vacuum, overnight. If time is short, a few hours in vacuum is usually sufficient. |

16. Re-weigh each capsule and its contents, so the mass fraction of water that had been adsorbed by the sample may be determined. Record the mass as that of the ‘Capsule plus test portion after drying.’

| Re-weighing should be done soon after the drying operation has been terminated. Re-hydration may be significant if a capsule stands in normal air for more than a short time. The dry masses of both samples may be calculated from the recorded data. |

**Special procedures:**

**Single test portion for both argon isotopic analysis and K determination:** When the test portion is used for argon extraction and isotopic analysis of argon is to be used also for K determination, high accuracy in weighing is not important. Omit steps 3, 4, and 9–12, and the amount to be weighed in step 7 is to be an amount appropriate for the argon work. Drying and re-weighing are also not important.

**Weighing of very small amounts:** If a test portion smaller than 10 mg is to be prepared, a special weighing procedure should be used for highest accuracy. Test portions smaller than 10 mg should be weighed at least three times to minimize weighing error. For such weighing, set the balance so that it will not automatically re-zero itself between weighings. **With no manual re-zeroing,** record the empty-pan reading of the balance before and after each weighing. First, weigh the empty capsule three or more times in this way, and then weigh the capsule with the test portion in it three or more times in this way.
Atomic Absorption Spectrophotometry B.2
GUIDELINES FOR DETERMINATION OF POTASSIUM IN ROCK AND SOIL BY FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

The following guidelines are for digestion of rock or soil materials for potassium determination, for preparation of test solutions for potassium determination by flame atomic absorption spectrophotometry (FAAS), for the instrumental procedure, and for subsequent calculations.

1. No special methods to avoid contamination are needed in potassium determination. Ordinary reagent grade chemicals may be used. Containers need not be pre-cleaned in acid solution. Used containers should be washed in detergent solution, rinsed thoroughly with tap water, and then rinsed with deionized water before they are used again.

2. The amount of rock or soil in a test portion to be used for potassium determination may range from less than 10 mg for K-rich material to more than 100 mg for K-poor material. In choosing the amount to use, consideration must be given to the accuracy of weighing and to the need for the test portion to be a good sample of the rock or soil whose K content is to be determined.

3. The error in weighing a test portion should be less that 1% of its mass, preferably much less. Note that readings from a balance that reads to 0.0001 g are not likely accurate to 0.0001 g. Test portions smaller than 10 mg should be weighed at least three times to minimize weighing error. For such weighing, set the balance so that it will not automatically re-zero itself between weighings. With no manual re-zeroing, record the empty-pan reading of the balance before and after each weighing of the test portion.

4. The mass of a clay-bearing material will include that of adsorbed water. Because the amount of adsorbed water depends on the humidity of air, an analyst must consider the effect of humidity before weighing such materials. In some kinds of work, clay-bearing material should be dried before weighing unless moisture content is determined independently. For K-Ar work involving two test portions (one for K determination and one for argon extraction and isotopic analysis), the best practice is to let the clay-bearing material reach equilibrium with the ambient air and to then weigh both test portions at about the same time.

5. Rock or soil for potassium determination is to be digested in a gently warmed mixture of concentrated HF and HNO\(_3\) in a closed PFA vial. After digestion overnight, the vial is opened, temperature is increased, and SiF\(_4\) and excess acids are evaporated away, leaving nitrate salts of the metals.

6. To provide a nearly uniform test-solution matrix, the test solutions for FAAS are to contain CsCl (0.01 mol/L) and HNO\(_3\) (0.1 mol/L). The CsCl and HNO\(_3\) will be by far the dominant substances in solution, providing a nearly uniform matrix. The presence of the Cs will minimize ionization interference, and the HNO\(_3\) will provide the acidity necessary to ensure that potassium remains in solution.

7. To prepare the acidic solution of CsCl, dissolve 1.68 g CsCl in roughly 50 mL of deionized water. Add 9.0 g (6.3 mL) concentrated HNO\(_3\) and dilute the mixture to 1000 mL with deionized water.

8. Although the amounts of CsCl and HNO\(_3\) in the acidic CsCl solution (also called “diluting solution”) are referenced to volume of solution, the amount of potassium in test solutions and reference solutions are to be expressed and recorded as mass fractions (having the unit mg/kg).
9. Polyethylene bottles are appropriate containers for the test solutions for potassium determinations. Polystyrene centrifuge tubes may also be used. Experience has shown that new containers of these types need not be pre-cleaned for potassium work.

10. A quantitative record of the mass of each test solution must be kept in all steps of preparation. The mass of each empty container with its lid should be measured and recorded before it is used, so that the mass of solution in the container can be determined at any stage of test-solution preparation. (An alternative is to use a tared balance for all solution weighings, but that requires careful advance planning when a set of test solutions is in preparation.)

11. The residual nitrate salts from digestion of rock or soil should be taken up in from 40 mL to 180 mL of the acidic CsCl solution. (Use a smaller volume if the K content of the soil or rock is likely to be very low.) Any of the test solutions may be further diluted later if necessary to bring the mass fraction of potassium into the appropriate range for accurate FAAS measurements. Potassium mass fractions in solution in the range 1 mg/kg to 2 mg/kg provide the best accuracy.

12. Reference solutions (“standards”) for potassium must be prepared to have the same concentrations of CsCl and HNO₃ (0.01 mol/L and 0.1 mol/L, respectively) as the test solutions. Several reference solutions having potassium mass fractions across the range where absorbance is a nearly linear function of potassium mass fraction (0 to 2.0 mg/kg) should be available.

13. Before beginning a set of potassium measurements by FAAS, use preliminary measurements of absorbance to find any solutions that need to be diluted to bring the mass fraction of K below 2.0 mg/kg.

14. Dilute a portion of each solution found to have more than 2.0 mg/kg potassium with the acidic CsCl solution to bring its K mass fraction to below 2.0 mg/kg. Weigh the portion of solution to be diluted before dilution, and then weigh the diluted solution, so the degree of dilution is accurately known.

15. For a set of measurements of potassium by FAAS, use preliminary measurements of absorbance to arrange the test solutions and reference solutions in a series in which each test solution is appropriately bracketed by two reference solutions (that is, so each test solution is between the reference solution having the nearest lower concentration of potassium and the one having the nearest higher concentration).

16. Program the instrument to take ten one-second readings of absorbance and return the average and standard deviation. The average will be considered one measurement of absorbance. Take at least three sets of absorbance measurements across the entire series (four sets or more is preferable for K-Ar work). The standard deviation of each set of ten absorbance readings should be noted (but not necessarily recorded) to ensure that aberrant values are not included in the results. If the standard deviation of a set of readings is more than about 2%, reject that set and take another set of ten readings.

17. For each set of absorbance readings, calculate the mass fraction of potassium in each test solution by interpolation, assuming that absorbance is a linear function of concentration across the concentration range of the two reference solutions that bracket the test solution.

18. For each test solution, calculate the average and standard deviation of the several values of K mass fraction calculated in the preceding step.
### Daily Start Up and Shut down B.3

#### DAILY STARTUP

1. Begin the daily chart record as follows:
   a. (Optional) Advance the chart and remove the record of previous work.
   b. Turn the chart drive on.
   c. Put the pen in place and lower it to record.
   d. Set the chart speed to 30 cm/h or less.
   e. Record the date, time, analyst (optional), and chart speed.

   *Use the chart to keep a written record of subsequent activity. If the analyst is careful to record all changes in chart speed (preferably along the left side of the chart), the chart will provide a useful time record of the work.*

   *If the recorder is on STBY, change to REC.*

   *The steps following this one are written on the assumption that the rough pump has been running at least overnight, valves R1 and R2 are open, and the turbomolecular pump is on.*

2. Read and record the pressure, $P_0$, in the rough pumping line.

   *$P_0$ should be less than 300 millitorr. A value persistently greater than that indicates either a leak or too much volatile material in the molecular sieve trap (which could be cooled to solve that problem).*

3. Read and record the pressure, $P_1$, in the argon extraction line.

   *The value of $P_1$ provides information about the state of the extraction line that may be important.*

4. Read and record the pressure, $P_2$, in the line between valve D2 and trap DT-2.

   *The value of $P_2$ before the trap DT-2 is cooled provides information about the state of the turbomolecular pumping line that may be important.*


   *Any water in the small Dewar flask should be removed before the liquid nitrogen is put in it. $P_2$ should be at or near zero soon after the trap is cooled.*

6. Check that the valves T2, T4, and V1 are closed.

7. Turn on the mass spectrometer as follows:
   a. Release the zero check button of the electrometer and set the electrometer to the $10 \times 10^{-11}$ A range.
   b. Set the mass selector on the MS-10 to the red 36 mark.
   c. On the MS-10 control panel, turn the Mains switch on and the Filament switch on.

   *The position where $m/z=40$ will be near but not necessarily exactly at the “red 36” mark.*

   *A signal should appear in about 20 s. A little argon invariably accumulates in the mass spectrometer overnight.*

8. Adjust the mass selector as necessary to the top of the $m/z = 40$ peak.

   *If there is no signal, likely because there is too much gas in the mass spectrometer, go to the next step.*


   *The driver should be turned counterclockwise at least two full turns but not more than three turns.*

10. Open valve T3.

    *The signal at $m/z = 40$ should decrease (but there may be a transient increase initially).*

11. Turn power on to the titanium heaters (TF-1 and TF-2).

    *The signal at $m/z = 40$ will increase temporarily as the titanium degasses. Allow 20 minutes for degassing before beginning an argon extraction.*

12. Open the valves D1 (if closed) and T0 (if any gas in the small Dewar flask should be removed before the liquid nitrogen is put in it. $P_2$ should be at or near zero soon after the trap is cooled.)
<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.</td>
<td>Open the valve, F1 or F2, that leads to the part of the line where argon extractions are to occur, if it is not already open. The response of P1 will depend largely on how much water was in the extraction line before valve T0 was opened. The other valve, F1 or F2, should be closed. Observe P1 and P2.</td>
</tr>
<tr>
<td>15.</td>
<td>Check that valves S2 and A2 are closed. Do not open any of these valves in the process of checking that they are closed (fully turned clockwise).</td>
</tr>
<tr>
<td>16.</td>
<td>Open valve S0. Then open, as appropriate for the intended work, valve A1 and/or valve S1. It is good practice to note the response of P1 and of the mass spectrometer to the opening of each of these valves.</td>
</tr>
</tbody>
</table>

### DAILY SHUTDOWN

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Turn off the mass spectrometer as follows: The shutdown procedures are for the typical situation in which a day’s work ends as an isotopic analysis of argon is completed. The electrometer is not to be turned off, unless the entire system is to be shut down for a long time.</td>
</tr>
<tr>
<td>a.</td>
<td>On the MS-10 control panel, turn the Filament and Mains switches off.</td>
</tr>
<tr>
<td>b.</td>
<td>Depress the zero check button of the electrometer.</td>
</tr>
<tr>
<td>2.</td>
<td>Check that valve T2 is closed. Close valve T3. Close valve D2 if it is not already closed. It is not necessary that the last argon sample be pumped out of the mass spectrometer before shutdown. There will be plenty of time for that on the next work day.</td>
</tr>
<tr>
<td>3.</td>
<td>Close valve S1 if it is open. Close valve A1 if it is open. Then close valve S0. Having these valves closed during periods of inactivity is important to the integrity of the reference gases.</td>
</tr>
<tr>
<td>4.</td>
<td>If valve T1 is open, close it.</td>
</tr>
<tr>
<td>5.</td>
<td>Stop the recorder as follows. The recorder is not normally turned off overnight. Optionally, it may be put on standby (STBY). The analyst may choose to remove the chart paper having the record of the day’s work, or not.</td>
</tr>
<tr>
<td>a.</td>
<td>Chart speed = off.</td>
</tr>
<tr>
<td>b.</td>
<td>Lift the pen, remove it, and put the cap over its tip.</td>
</tr>
</tbody>
</table>
### DISSOLUTION OF SILICATE MATERIALS FOR POTASSIUM DETERMINATION

<table>
<thead>
<tr>
<th>Step</th>
<th>Instructions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pour 5–10 of a 10:3 (mass ratio) mixture of concentrated HF and concentrated HNO₃ into a clean fluorocarbon beaker.</td>
<td>The acid mixture may be made by mixing 500 g concentrated HF with 150 g concentrated HNO₃.</td>
</tr>
<tr>
<td>2.</td>
<td>Use a disposable bulb pipette to add 0.5 ml of the acid mixture to each test portion in its PFA vial. Add the same amount to an empty vial for a blank measurement.</td>
<td>If the mass of a sample is more than about 50 mg, use 1 ml of the acid mixture for each 100 mg of the sample. (Discard the unused acid mixture; do not return it to the original bottle.)</td>
</tr>
<tr>
<td>3.</td>
<td>Close the PFA vials securely and heat them gently (not more than 100°C) overnight.</td>
<td>Heating for just a few hours should be sufficient for clay to be digested.</td>
</tr>
<tr>
<td>4.</td>
<td>Remove the closed vials from the heat source. Wait at least 5 minutes and then tilt and tap each one so that drops of condensate on the lid run down into the container.</td>
<td>HF solution condensed on the inside of the lids poses a hazard for skin and laboratory surfaces. When a vial is opened, be careful that no drops fall from the lid or run down the outside of the vial.</td>
</tr>
<tr>
<td>5.</td>
<td>Open each vial and place the vial and its cap on a hot plate in a fume hood.</td>
<td>The temperature should be set to about 120°C, appropriate for slow evaporation of the liquid, driving off SiF₄, HF, H₂O, and HNO₃.</td>
</tr>
<tr>
<td>6.</td>
<td>Continue heating each vial until all or nearly all of the liquid has evaporated away.</td>
<td>Since HF is more volatile than HNO₃, the residue will be largely solid nitrate salts of metallic elements. These salts are readily soluble. If the hot plate is too hot, however, nitrates may decompose, leaving some oxides that are not readily soluble.</td>
</tr>
<tr>
<td>7.</td>
<td>Partially fill each vial with cesium-bearing diluting solution and close it securely (preferably with the same lid used during the digestion).</td>
<td>The diluting solution contains CsCl (0.01 mol dm⁻³) and HNO₃ (0.1 mol dm⁻³). It is used for dissolving and diluting the residues of the acid digestion and for preparing the reference solutions used in potassium determination.</td>
</tr>
<tr>
<td>8.</td>
<td>Heat each vial gently and shake as necessary until the solids are dissolved.</td>
<td>Minor amounts of undissolved accessory minerals or organic matter resistant to digestion may be ignored, for their potassium content will be negligible.</td>
</tr>
<tr>
<td>9.</td>
<td>Label and weigh a capped bottle to which the contents of each vial will be transferred. Record the mass of the capped bottle.</td>
<td>4 ounce (125 ml) or 6 ounce (180 ml) polyethylene bottles are normally used. Smaller bottles (1 oz or 2 oz) might be used for blanks or for materials expected to have very little K.</td>
</tr>
<tr>
<td>10.</td>
<td>Warm the PFA vials (if they are not still warm from step 8) in preparation for step</td>
<td>Warm PFA is less likely than cool PFA to retain some of the solution on its surface.</td>
</tr>
<tr>
<td>11.</td>
<td>Transfer the solution in each PFA vial to the bottle prepared for it.</td>
<td>If there are undissolved solids, avoid transferring them with the liquid. Use a bulb pipette for the transfer if necessary.</td>
</tr>
<tr>
<td>Step</td>
<td>Description</td>
<td>Additional Information</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>12.</td>
<td>Examine undissolved material remaining in any PFA vial. If more than a minor amount of mineral or organic matter remains in a vial, add 0.5 ml of the HF-HNO₃ acid mixture to the vial and repeat steps 3–8, 10, and 11 for it.</td>
<td>It is not likely that undissolved materials will contain a significant amount of potassium, so minor amounts are not a concern. A second digestion is called for if the analyst is not confident that K-bearing silicates were completely dissolved.</td>
</tr>
<tr>
<td>13.</td>
<td>Rinse each PFA vial at least once with the diluting solution, adding the rinse solution(s) to the appropriate bottle.</td>
<td>One rinse is sufficient if all the liquid poured out of the PFA vial during the transfer (Step 11). Otherwise, rinse twice.</td>
</tr>
<tr>
<td>14.</td>
<td>Use the diluting solution to bring the material in each polyethylene bottle to an appropriate volume. Cap the bottle and shake it to homogenize the solution.</td>
<td>In most cases, the appropriate volume will be that of a nearly full bottle. In cases where the amount of potassium is expected to be much less than normal (a blank run, for example), a volume smaller than that of a full bottle would be appropriate.</td>
</tr>
<tr>
<td>15.</td>
<td>Weigh the capped bottle and its contents and record the mass.</td>
<td></td>
</tr>
</tbody>
</table>
Extraction by Fusion, Isotope Dilution, Cleanup and Isotopic Analysis of Argon B.5

**EXTRACTION BY FUSION, ISOTOPE DILUTION, CLEANUP, AND ISOTOPIC ANALYSIS OF ARGON**

### Setup Check
This checklist is to see that the extraction line and mass spectrometer are correctly set up for gas extraction by fusion, isotope dilution, cleanup, and isotopic analysis of argon.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbomolecular pump running at 75 K RPM</td>
<td>Normally, valves R1 and R2 will be open when the turbomolecular pump is running. See separate instructions for operation of the pumping line.</td>
</tr>
<tr>
<td>1. Liquid nitrogen on trap DT-2</td>
<td></td>
</tr>
<tr>
<td>2. Valves D1, D2, T0, T1, F1, S0, and S1 open</td>
<td>Valve T3 is always open.</td>
</tr>
<tr>
<td>3. Valves V1, C2, <strong>F2, T2</strong>, T4, A1, S2, and S3 closed</td>
<td>Certain other valves, in particular A2 and S4, will also be closed, but their status does not need to be checked. Boldface indicates valves most likely to have been left open. <strong>Be sure not to open S2 in checking its closure.</strong></td>
</tr>
<tr>
<td>4. Titanium heaters TF-1 and TF-2 hot</td>
<td>The titanium heaters should have been hot for at least 20 minutes before proceeding. This is to ensure that they have been well degassed.</td>
</tr>
<tr>
<td>5. P1 less than 10 mTorr and P2 less than 1 mTorr</td>
<td></td>
</tr>
<tr>
<td>6. Mass spectrometer on and set for m/z = 40, near Red 36</td>
<td>The signal at m/z = 40 should be low on the $0.1 \times 10^{-11}$ A range, as it will be if the system has been well degassed and there are no leaks.</td>
</tr>
<tr>
<td>7. Cooling water flowing at about 5 mL/s</td>
<td></td>
</tr>
</tbody>
</table>

### Argon Extraction, Isotope Dilution, and Cleanup

<table>
<thead>
<tr>
<th>Step</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Put liquid nitrogen in the cold finger of trap MT-1.</td>
<td>When the liquid nitrogen has stopped rapid boiling, the cold finger should be about one-half filled.</td>
</tr>
<tr>
<td>2. Put liquid nitrogen, in a small Dewar flask, around MT-1. [Do not proceed to step 3 if argon is being pumped from the mass spectrometer in a &quot;Mass Spectrometer Setup&quot; procedure, below.]</td>
<td>The level of liquid nitrogen in the Dewar flask should be a little less than that in the cold finger.</td>
</tr>
<tr>
<td>3. Prepare the spike by closing valve S1 firmly and then opening valve S2.</td>
<td>The underlining is to emphasize the importance of <strong>not having both S1 and S2 open at the same time.</strong></td>
</tr>
<tr>
<td>4. Close valve T0.</td>
<td>This important step isolates the extraction line from the pumps. The “Mass Spectrometer Setup” below may begin at any time after T0 has been closed.</td>
</tr>
<tr>
<td>5. Drop the capsule into the furnace.</td>
<td>Be careful that the “capsule pusher” doesn’t fall into the furnace.</td>
</tr>
</tbody>
</table>
6. Turn on power to the furnace. This is done by raising the variable transformer setting to 20. A magnet may be used to check that current is flowing.

7. Release the spike by closing valve S2 firmly and then opening valve S1. The underlining is to emphasize the importance of not having both S1 and S2 open at the same time. Record the spike number on the chart.

8. Turn the fan on.

9. Connect the chart recorder to P1. If an isotopic analysis is in progress, wait until the isotopic analysis is finished to begin recording the P1 pressure reading.

10. At intervals of one minute or longer, raise the power to the furnace in steps of five units on the variable transformer. It is good practice to observe the interior of the furnace after each increase in power. It is useful to see when the copper capsule melts and to observe the behavior of the silicate material as it melts.

11. After the variable transformer has been set for the maximum power to be used, hold at that setting for five minutes. The maximum transformer setting is currently 50. The maximum power may be held for up to ten minutes, but five minutes is sufficient for most materials.

12. Turn off power to the furnace. This is done by turning the variable transformer to zero.

13. Turn the fan off.

14. Wait two minutes and then turn off power to the titanium heater TF-1. A one-minute wait is sufficient if P1 is below 30 mTorr after the first minute.

15. Wait two more minutes and then put liquid nitrogen on the charcoal, CC-1. A one-minute wait is sufficient if P1 is below 30 mTorr after the first minute. Make sure the liquid nitrogen level is above the glass wool above the charcoal.

16. Put liquid nitrogen in the cold finger of trap MT-2. Adjust the height of the liquid nitrogen to between 1 and 2 cm. Wait until P1 is below 20 mTorr before putting the liquid nitrogen in the cold finger.

17. Move the Dewar flask of liquid nitrogen that is on MT-1 to MT-2. The outside of MT-1 may be washed with ethanol to reveal the ice ring(s) from the volatiles condensed on the cold finger.

18. Remove any liquid nitrogen that is in the cold finger of MT-1. Use a large Teflon stirring rod to ‘heat’ the liquid nitrogen so that it evaporates. Then turn the rod around to so that its warm end helps the cold finger warm up rapidly.

19. Watch P1 to observe the movement of volatiles from the MT-1 cold finger to the MT-2 cold finger. Proceed only after P1 has returned to below 30 mTorr after the peak of H2O transfer. Evaporation of ices from the cold finger of MT-1 releases any argon that may have been trapped in them.


21. Remove the liquid nitrogen from CC-1. Be very careful not to break the glass.

**Argon Transfer**

1.
1. Connect the chart recorder to the electrometer output to record the signal from the mass spectrometer.

2. If not already so set, set the mass spectrometer to \( m/z = 40 \) with the electrometer on the \( 0.1 \times 10^{-11} \) A range. The signal at \( m/z = 40 \) should be low on the \( 0.1 \times 10^{-11} \) A range, as it will be if the system has been well degassed and there are no leaks.

3. Close valve D2. The signal at \( m/z = 40 \) normally rises somewhat when D2 is closed.

4. Set the electrometer to the \( 10 \times 10^{-11} \) A range.

5. Open valve T2 Observe the signal at \( m/z = 40 \). If it should rise above full scale, change to the \( 10 \times 10^{-10} \) A range.

6. Wait 1.5 minutes and then close T2.

7. Turn off power to TF-2. If there is little or no signal at \( m/z = 40 \) at this point, because a relatively large amount of gas is overwhelming the ion beam of the mass spectrometer, a special procedure may be needed to allow the getters to react with the non-inert gases present.

### Isotopic Analysis of Argon

1. Set the mass selector to below \( m/z = 36 \) (at Red 25), set the electrometer to the \( 0.1 \times 10^{-11} \) A range, and scan over \( m/z = 36 \) one or more times to confirm that pressure is low enough for accurate measurement of the argon isotopes. When pressure is sufficiently low, the baseline for the \( m/z = 36 \) peak will be stable and will not be steeply sloped. Early on, it is normal for the baseline to decrease in level and in slope as the cooling titanium in TF-2 absorbs hydrogen (which scatters some ions from intense ion beams (of \(^{40}\text{Ar}, ^{38}\text{Ar}, \) and residual gases such as \( \text{CO}_2 \) and \( \text{N}_2 \)) so that they go through the collector slit of the mass spectrometer even when undeflected ions from the intense beams are well away from the slit).

2. Take two sets of measurements of the argon isotopes, each set consisting of a scan upward through the mass range and then a scan of the peaks in reverse order. Choose the most sensitive electrometer range possible for each isotope. Be sure to get the baseline on each side of each 36 peak, and similarly for at least one of the 38 peaks and one of the 40 peaks in each of the two sets of measurements.

3. When the isotopic measurements are done, go to “Mass Spectrometer Setup,” below.

   “Mass Spectrometer Setup” may begin at any time after step 4 of “Argon Extraction, Isotope Dilution, and Cleanup” has been completed for the next run. (It can be done earlier if the operator takes special care to see that argon coming out of the mass spectrometer does not get mixed with argon, from sample or spike, of the next run.) There is no need to do the setup after the last run before shutdown.

### Extraction Line Setup

2. Open valve T0.
3. Remove the Dewar flask of liquid nitrogen from MT-2.  
   *The outside of MT-2 may be washed with ethanol to reveal the ice ring(s) from the volatiles condensed on the cold finger.*

4. Remove any remaining liquid nitrogen from the MT-2 cold finger.

5. Turn on power to TF-1.

6. After water from MT-2 has been pumped away (P1 < 20 mTorr), open valve T1.

   **Wait at least three minutes for the extraction line to become fully evacuated before beginning “Argon Extraction and Cleanup” (above) for the next sample.**

   TF-1 should be hot before beginning “Argon Extraction and Cleanup” for the next sample. That may mean waiting more than three minutes.

---

**Mass Spectrometer Setup**

1. Turn on power to titanium heater TF-2.

2. Set the mass selector to \( m/z = 40 \).  
   *The electrometer should be set to a range appropriate for the signal.*

3. Check that there is sufficient liquid nitrogen on trap DT-2.

4. Open valve D2.

   **Wait at least three minutes for the argon in the mass spectrometer to be evacuated before beginning the next argon transfer.**
Appendix C: XRD Patterns

Reference Fallout Material C.1

XRD Pattern of reference fallout material 2-21 (each $d$ value is for the peak directly above or under the corresponding “d”).
XRD Pattern of reference fallout material 8-6 (each $d$ value is for the peak directly above or under the corresponding “$d$”).
XRD Pattern of reference fallout material 8-36 (each d value is for the peak directly above or under the corresponding “d”).
Kyoto Dust 3.4 XRD pattern (each $d$ value is for the peak directly above or under the corresponding “d”).
Kyoto Dust 5.6 XRD pattern (each $d$ value is for the peak directly above or under the corresponding “$d$”).
5-20µm Mt. Daisen Soil Patterns for Slide Mounts C.3

1A 5-20 µm oriented slide XRD patterns (each $d$ value is for the lavender peak directly above or under the corresponding “$d$”).
1B 5-20 µm oriented slide XRD patterns (each $d$ value is for the blue peak directly above or under the corresponding “d”).
2A 5-20 µm oriented slide XRD patterns (each \( d \) value is for the green peak directly above or under the corresponding “d”.

2B 5-20 µm oriented slide XRD patterns (each $d$ value is for the green peak directly above or under the corresponding “d”).
3A 5-20 µm oriented slide XRD patterns (each \(d\) value is for the blue peak directly above or under the corresponding “d”).
<2 µm Mt. Daisen Soil Patterns C.4

2A <2 µm oriented slide XRD patterns (each $d$ value is for the red peak directly above or under the corresponding “d”).
3A <2 µm oriented slide XRD patterns (each $d$ value is for the lavender peak directly above or under the corresponding “d”).
5-20µm Mt. Daisen Soil Patterns for Randomly Packed Powder C.5

1A 5-20 µm powder XRD pattern (each \( d \) value is for the peak directly above or under the corresponding “\( d \)”).
2A 5-20 µm powder XRD pattern (each $d$ value is for the peak directly above or under the corresponding “d”).
3A 5-20 µm powder XRD pattern (each $d$ value is for the peak directly above or under the corresponding “$d$”).